A STUDY OF THE PRODUCTS OBTAINED BY A FRIEDEL-CRAFTS REACTION OF PROPYLENE OXIDE WITH CUMENE

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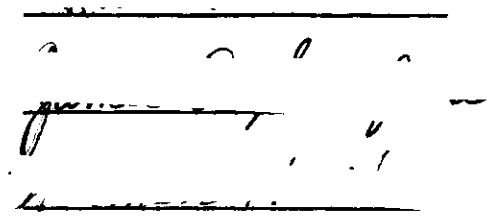

Date Approved by Chairman:

June 3 1954

FOREWORD

I wish to express my sincere appreciation to Mr. N. H. Horton for his suggestions and patience during the pursuit of this problem.

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SUMMARY

The purpose of this work was to carry out the reaction of propylene oxide with cumene in the presence of aluminum chloride under conditions favorable to the formation of alcohols. The alcohol products were to be identified. Some physical properties of the alcohols and of compounds produced by reactions of the alcohols were to be determined.

The reaction of propylene oxide with cumene was carried out in the following way. To a mixture of 4.9 moles of cumene and 1.1 moles of anhydrous aluminum chloride was slowly added a solution of one mole of propylene oxide in 4.9 moles of cumene while reaction temperature was maintained at 0-10°C. About one hour after completion of the addition the reaction mixture was hydrolyzed with ice water. The organic layer was separated from the water layer, washed free of acid, and dried with anhydrous sodium sulfate. Unreacted cumene was distilled and the remaining product fractionated under vacuum. Alcohol products were obtained in yields to 64.6 per cent of theory, based on propylene oxide.

Two main products were indicated by the initial fractionations of the products from five preparations. The lower boiling product was identified as m-isopropyl-β-

methylphenethyl alcohol. The higher boiling product was p-isopropyl-β-methylphenethyl alcohol. Careful refractionations of the two alcohol products failed to yield uncontaminated products.

The physical properties of a middle fraction of m-isopropyl-β-methylphenethyl alcohol were as follows:

Boiling point = 101.6°C. at 3mm. Hg.
Refractive index n_D^{25} = 1.5135
Density d_4^{25} = 0.9583.

A middle fraction of p-isopropyl-β-methylphenethyl alcohol had the following physical properties:

Melting point = 43.5-44.5°C.
Boiling point = 103.3°C. at 3mm. Hg.
Refractive index n_D^{25} = 1.5130.

Fractional recrystallization of the O-alkylsaccharin derivative of m-isopropyl-β-methylphenethyl alcohol yielded two portions with melting ranges of 107-115°C. and 183.5-184.0°C. The O-alkylsaccharin derivative of p-isopropyl-β-methylphenethyl alcohol had a melting point of 166.5-168.2°C.

Vigorous oxidation of the two alcohols yielded their corresponding phthalic acids. Mild oxidation with di-t-butyl chromate gave the corresponding aldehydes in good yields. The aldehyde prepared from m-isopropyl-β-methylphenethyl alcohol had the following physical properties:

Boiling point = 87.2°C. at 3.5mm. Hg.

Refractive index n_D^{25} = 1.5076

Density d_4^{25} = 0.9609.

The aldehyde prepared from the para alcohol had the following physical properties:

Boiling point = 84.8°C. at 2.5mm. Hg.

Refractive index n_D^{25} = 1.5102

Density d_4^{25} = 0.9558.

A solid acid was also produced during the mild oxidation of the para alcohol. It had a melting point of 71-74°C. and neutralization equivalent of 194. Oxidation of the para aldehyde with basic permanganate gave the same acid with a melting point of 71.0-73.5°C. and a neutralization equivalent of 194. The acid produced from oxidation of the meta aldehyde was an uncrystallizable oil.

Dehydration of the alcohols with molten potassium hydroxide produced the corresponding styrene derivatives. The olefin produced from the dehydration of the meta alcohol had the following physical properties:

Boiling point = 213.6°C. at atmospheric pressure

Refractive index n_D^{25} = 1.5195

Density d_4^{25} = 0.8838.

The *para* alcohol yielded an olefin with the following physical properties:

Boiling point = 221.0°C. at atmospheric pressure

Refractive index n_D^{25} = 1.5228

Density d_4^{25} = 0.8851.

Some low boiling material produced during the preparation of the alcohols was found to be a mixture of isomeric di-iso-propyl-benzenes. Several unsuccessful attempts were made to identify O-isopropyl-β-methylphenethyl alcohol in the products of the reaction of propylene oxide with cumene.

HISTORY

The reaction of alkylene oxides with aromatic compounds, in the presence of Friedel-Crafts type catalysts, has been reported in several papers.

Ethylene oxide has been reported to react with benzene[1,2,3,4], toluene[5,6,7], ethylbenzene[5,6], xylenes[5,6,7], biphenyl[8], naphthalene[9], tetrahydronaphthalene[9], anisole[5], chlorobenzene[7], and bromobenzene[2]. In all cases aluminum chloride was used as the Friedel-Crafts catalyst. When the

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[1] A. Schaarschmidt, L. Hermann, and B. Szemzo, Ber., 58, 1914 (1925).

[2] R. A. Smith and S. Natelson, J. Am. Chem. Soc., 53, 3476 (1931).

[3] J. Colonge and P. Rochas, Bul. soc. chim. France, 1948, 818.

[4] T. Inatsugi, J. Soc. Org. Synthetic Chem., 7, 5 (1949).

[5] J. Colonge and P. Rochas, Compt. rend., 223, 403 (1946).

[6] J. Colonge and P. Rochas, Bull. soc. chim. France, 1948, 822.

[7] N. V. Shorygina, J. Gen. Chem. U.S.S.R., 21, 1391 (1951).

[8] J. Colonge and P. Rochas, Bull. soc. chim. France, 1948, 825.

[9] J. Colonge and P. Rochas, Bull. soc. chim. France, 1948, 827.

reactions were carried out in the range of 0-10° C., beta-substituted ethyl alcohols were the usual products. At higher reaction temperatures dibenzyl type compounds occurred.

The reaction of benzene with propylene oxide has been reported to produce the secondary alcohol alpha-methylphenethyl alcohol and methyldibenzyl.[10] However, a patent states that the alcohol product is beta-methyl-phenethyl alcohol.[11] The latter product seems to be the correct one.

The reactions of some aromatic hydrocarbons with a number of alkylene oxides have been described by Theimer.[12] He found that all alkylene oxides containing one unsubstituted carbon of the epoxy ring reacted with aromatic compounds to produce primary alcohols. Alkylene oxides with both carbons of the epoxy ring substituted produced low yields of secondary alcohols.

Several patents have been issued on processes for the production of alcohols by the reaction of alkylene

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[10] Smith and Natelson, loc. cit.

[11] E. T. Theimer, U. S. Patent 2,047,396 (1936).

[12] E. T. Theimer, Abstract of A.C.S. Meeting, April 1940.

oxides with aromatic compounds.[13] Some of the aromatic compounds used as reactants are benzene, toluene, cymene, chlorobenzene, anisole, acetophenone, benzophenone, benzaldehyde, tolualdehyde, diphenyl ether, and naphthalene. The alkylene oxides include ethylene, propylene, trimethylene, and isobutylene oxides. In most of the patents an excess of the aromatic compound and of the Friedel-Crafts catalyst is specified. Highest yields of alcohol products are claimed with reaction temperatures below 10°C.

Somerville and Spoerri[14] have studied the reactions of some disubstituted ethylene oxides. The reaction of 2,3-butylene oxide with benzene produced low yields of 3-phenylbutanol-2 and 2,3-diphenylbutane. Under similar reaction conditions isobutylene oxide and benzene produced low yields of 2-methyl-2-phenylpropanol and two hydrocarbons.

The mechanism[15] of the reaction seems to involve ring opening of the epoxide I by the catalyst to form the secondary carbonium ion II. The carbonium ion then reacts

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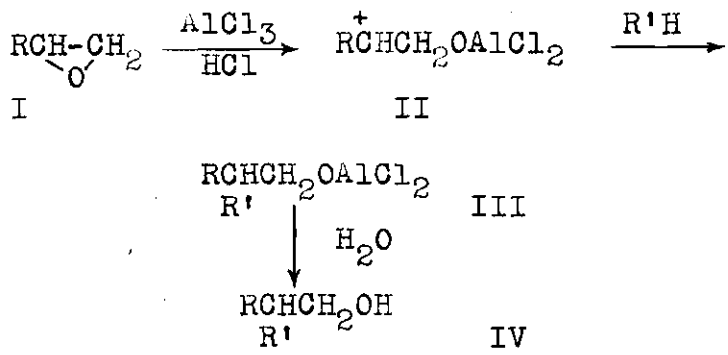
[13]M. S. Carpenter, U.S. Patent 2,013,710 (1935); H. S. Davis, U.S. Patent 2,125,490 (1938); I. G. Farbenind. A.-G., Brit. Patent 354,992 (1931); I. G. Farbenind. A.-G., Ger. Patent 594,968 (1934); H. Hopff, U.S. Patent 2,029,618 (1936); K. H. Klipstein, Can. Patent 340,555 (1934); E. T. Theimer, U.S. Patent 2,047,396 (1936); E. T. Theimer, U.S. Patent 2,125,968 (1938); L. Valik and I. Valik, Brit. Patent 398,136 (1931).

[14]W. T. Somerville and P. E. Spoerri, J. Am. Chem. Soc., 72, 2185 (1950).

[15]W. T. Somerville and P. E. Spoerri, J. Am. Chem. Soc., 73, 697 (1951).

with the aromatic compound to produce the aluminum chloride salt III of the alcohol. The alcohol IV is produced by hydrolysis of the salt.



From previous reports of the reaction of alkylene oxides with aromatic compounds it can be said that alcohol products are usually obtained when the reaction is carried out at temperatures in the range of 0 to 10°C. Alkylene oxides having one unsubstituted carbon in the epoxy ring react at low temperatures to produce primary alcohols. At higher temperatures the products are usually those obtained by the reaction of two molecules of the aromatic compound with one of the alkylene oxide. Highest yields of alcohols are obtained when an excess of both the aromatic compound and the catalyst are used.

EXPERIMENTAL

GENERAL PROCEDURE

Chemicals.--Eastman's white label cumene was fractionated over sodium and the middle fraction boiling at constant temperature was stored over sodium wire. The refractive index of the purified cumene was 1.4882 at 25°C. The reported refractive index of cumene is 1.48890 at 25°C.[16] This method of storing cumene was abandoned after Run 2 because of the strongly basic precipitate that developed in the cumene upon exposure to air. Recovered cumene, with a boiling point of 83°C. at a pressure of 72 mm. of mercury and having a refractive index of 1.4882 at 25°C., was used in Run 3. Cumene obtained from Dow Chemical Company was dried over Drierite and fractionated for use in Runs 4 and 5. It had a refractive index of 1.4910 at 20°C. The reported refractive index of cumene at this temperature is 1.49145.[16] No differences in the reactions were noted using cumene obtained from the different sources.

The propylene oxide used in Runs 1 and 2 had been fractionated and stored in a refrigerator for several months. The propylene oxide used in Runs 3, 4, and 5 was fractionated and the middle fraction boiling at a constant

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[16]A. F. Forziati, J. Research Natl. Bur. Standards, 44, 383 (1950).

temperature of 34°C. was collected and stored at room temperature. It had a refractive index of 1.3670 at 20°C. The reported boiling point and refractive index of propylene oxide are 34°C. and 1.3664, respectively.[17]

The aluminum chloride used in all the reactions was taken from one pound bottles of Baker's Anhydrous Aluminum Chloride and used without further purification.

Run 1.--Into a two liter three-necked flask, fitted with a stirrer, thermometer and dropping funnel, was added 696 ml. (589 g., 4.9 moles) of cumene and 146.2 g. (1.1 moles) of anhydrous aluminum chloride. The flask was immersed in an ice bath. Into the dropping funnel was added 696 ml. (589 g., 4.9 moles) of cumene and 69 ml. (58.1 g., 1.0 moles) of propylene oxide. After the temperature of the mixture in the flask had dropped to 5°C., the slow addition of the contents of the dropping funnel was begun. The rate of addition was regulated to keep the temperature of the reaction mixture between 6 and 7°C. The color of the mixture in the flask changed from grey to yellow then to green during the addition. The addition was complete in one hour twenty-five minutes, and stirring was continued for an additional one hour thirty minutes during which time the temperature slowly dropped to 1°C. The reaction mixture

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[17]M. T. Rogers, J. Am. Chem. Soc., 69, 2544 (1947).

was poured onto 300 ml. of water and 700 g. of ice, with vigorous stirring. After the ice melted, the oil and water mixture was poured into a three liter separatory funnel, shaken thoroughly, allowed to settle, and separated. The organic layer was washed successively with 100 ml. of water, 100 ml. of a five per cent solution of sodium carbonate, and then with 100 ml. of a dilute solution of sodium chloride. The sodium chloride was added to the last wash solution to speed the separation of the two layers. The organic layer was dried with anhydrous sodium sulfate over night. The sodium sulfate drying agent was filtered from the solution of the product and washed with one portion of 100 ml. of cumene. The excess cumene was distilled off at a pressure of 72 mm. of mercury. Thirteen hundred twenty-two ml. of material boiling from 50-80°C. was collected, of which 1110 ml. were pure cumene boiling at 80°C. and having a refractive index of 1.4882 at 25°C.

The products from the reactions of cumene and propylene oxide were vacuum fractionated in a Todd[18] column 90 cm. long and 12 mm. in diameter. The column was packed with Podbielniak's Heli-Pak No. 2917 random packing. The vacuum fractionations were carried out with the column connected to a pressure regulator controlled by a manostat operating a leak valve. The take-off assembly was designed

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[18]F. Todd, Ind. Eng. Chem., Anal. Ed., 17, 175 (1945).

to allow changing of receivers without disturbing the pressure while operating under vacuum.

The 120 g. of product was transferred to a 200 ml. flask and fractionated at a pressure of 3.5 mm. of mercury. The fractionation data are given in Table 1.

A plot of the weight of product against the distilling temperature, Figure 1, indicates two products from the reaction of cumene and propylene oxide. The total yield of product, based on one mole of propylene reacted with one mole of cumene, was 48.9 per cent of theory. The yield of the lower boiling material, calculated from the rectification curve, was 54.0 per cent of the total yield.

Run 2.--The same general procedure and the same amounts of chemicals were used in this run as in Run 1. During the preparation of the cumene-propylene oxide mixture it was noted that the cumene, previously stored over sodium wire, became cloudy when exposed to air. A precipitate was apparent in few minutes and was found to be strongly basic. The addition of the contents of the dropping funnel required one hour thirty minutes with the temperature remaining between 8 and 10°C. The stirring was continued for an additional one hour thirty minutes during which the temperature slowly dropped to 2°C. After separation of the two layers, the organic layer was washed successively with 100 ml. of water, 100 ml. of a 5 per cent solution of

Table 1. Fractionation of Product from Run 1

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
1	-61	6	3.1	
2	61-66	"	4.7	
3	61-90	3.5	6.8	
4	90-106.5	"	7.9	
5	106.5-107	"	10.4	1.5108
6	107-108	"	34.5	1.5126
7	108-108	"	49.1	1.5128
8	108-110	"	53.2	1.5120
9	110-111	"	57.3	1.5118
10	111-112	"	60.5	1.5119
11	112-112	"	83.0	1.5119
12	112-112	"	95.1	1.5118

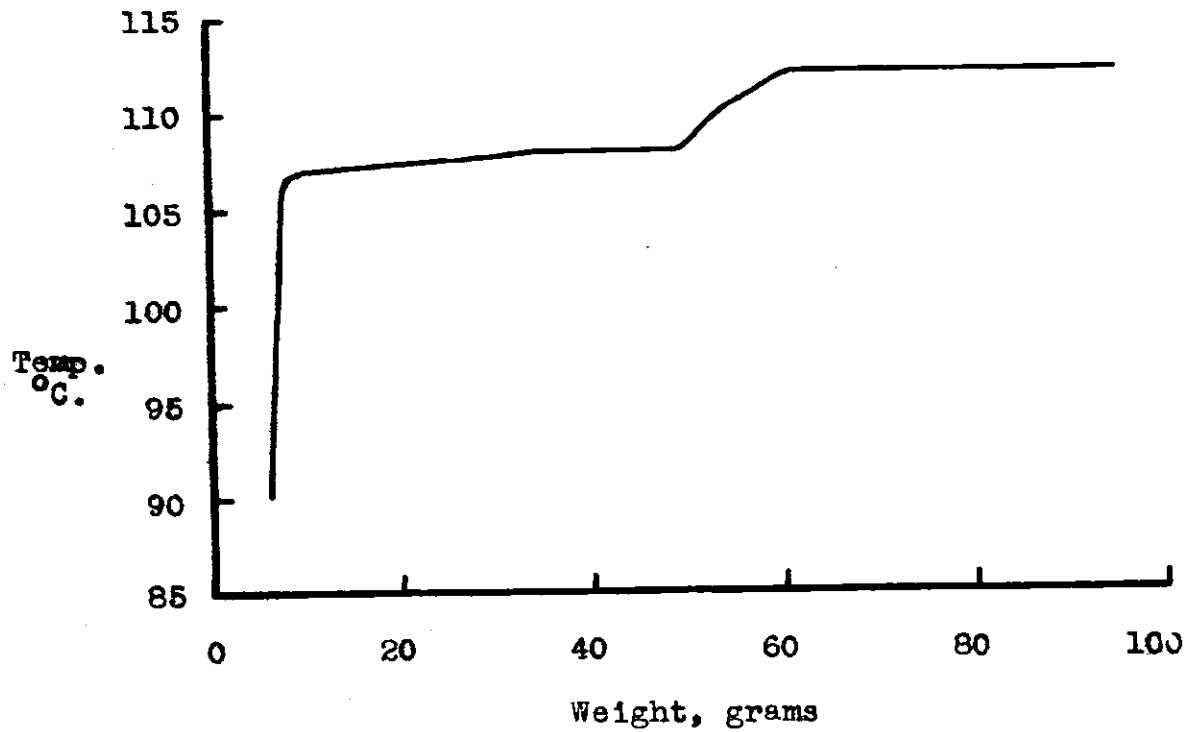

Figure 1. Run 1 Rectification Curve

sodium carbonate, and again with 100 ml. of water. The organic layer was then dried with anhydrous sodium sulfate over the weekend. The drying agent was removed by filtration, washed, and the excess cumene was distilled as in Run 1. The remaining product was fractionated at a pressure of 3.5 mm. of mercury, Table 2. The rectification curve, Figure 2, indicates two main products from the reaction of cumene and propylene oxide. The total yield of product, based on one mole of propylene oxide, was 55.6 per cent of theory. The yield of lower boiling material, calculated from the rectification curve, was 55.3 per cent of the total yield.

Fraction 3, boiling at 59°C. and having a refractive index of 1.4873 at 25°C., was believed to be 1,3-di-iso-propyl-benzene. The boiling point[19] at 3.5 mm. of mercury and the refractive index[20] at 25°C. of 1,3-di-iso-propyl-benzene are 59°C. and 1.48748, respectively.

Run 3.--The same general procedure and the same amounts of chemicals were used in this run as in Run 1. The temperature of the reaction was maintained at or below 5°C. by the addition of the contents of the dropping funnel over a period of three hours. Stirring was continued for one hour

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[19]D. R. Stull, Ind. Eng. Chem., 39, 532 (1947).

[20]F. W. Melpolder, J. E. Woodbridge and C. E. Headington, J. Am. Chem. Soc., 70, 935 (1948).

Table 2. Fractionation of Product from Run 2

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
1	-50	3.5		
2	50-59	"	12.2	1.4870
3	59-59	"	26.0	1.4873
4	59-60.5	"	33.3	1.4883
5	60.5-62	"	35.4	1.4890
6	62-100.5	"	37.4	1.5020
7	100.5-105	"	37.8	1.5088
8	105-106	"	39.0	1.5108
9	106-106.2	"	41.2	1.5113
10	106.2-107	"	43.3	1.5116
11	107-107.1	"	49.1	1.5118
12	107.1-107.1	"	56.3	1.5120
13	107.1-107.1	"	67.1	1.5126
14	107.1-107.2	"	72.1	1.5125
15	107.2-107.4	"	78.6	1.5127
16	107.4-107.4	"	87.5	1.5127
17	107.4-107.6	"	89.2	1.5125
18	107.6-110	"	93.8	1.5128
19	110-111.5	"	99.7	1.5121
20	111.5-112	"	121.2	1.5122
21	112-112	"	135.1	1.5125
22	112-112	"	138.1	1.5118

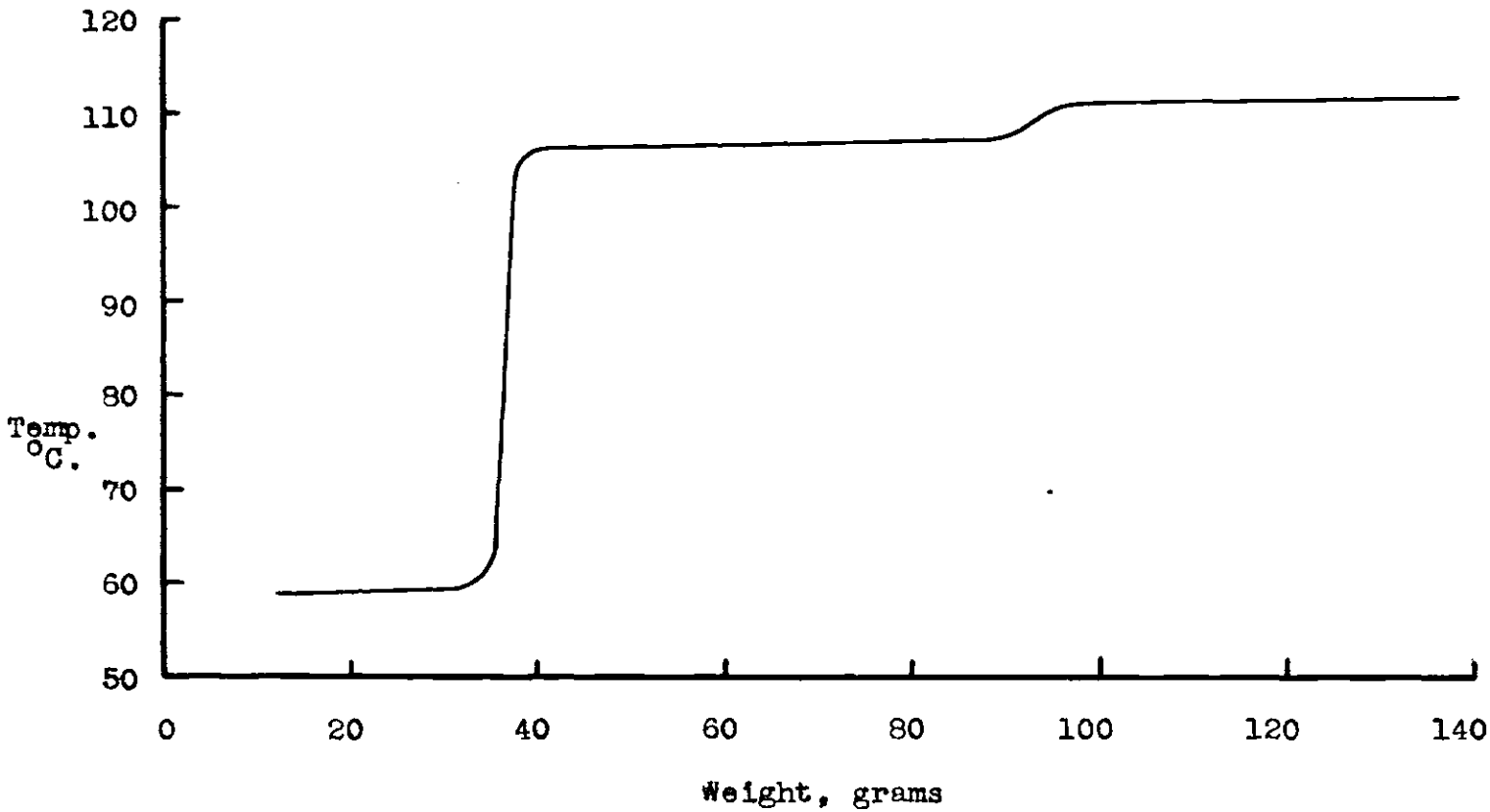

Figure 2. Run 2 Rectification Curve

thirty minutes after completion of the addition. After the separation of the two layers, the water layer was extracted with 50 ml. of cumene and the extract was added to the organic layer. The organic layer was then washed and dried in the same manner as in Run 2. The drying agent was filtered from the solution of the product and washed once with 50 ml. of cumene. Excess cumene was distilled at a pressure of 37 mm. of mercury. The remaining product was fractionated into 63 fractions at about 5 mm. of pressure, Table 3. The rectification curve, Figure 3, indicates two main products from the reaction of cumene with propylene oxide. The total yield of product, based on one mole of propylene oxide, was 59.1 per cent of theory. The yield of lower boiling material was 53.7 per cent of the total yield.

Fractions 2 through 19 were identified as mixtures of isomeric di-iso-propyl-benzenes. The boiling point[21] at a pressure of 5 mm. and the refractive index[22] at 25°C. of 1,2-di-iso-propyl-benzene are 67.8°C. and 1.49373, respectively. They are 62.3°C. and 1.48748 for 1,3-di-iso-propyl-benzene, and 70.1°C.[22] and 1.48983 for 1,4-di-iso-propyl-benzene.

The infrared spectra of fraction 11 was determined from 10 to 14.5 microns wavelength using a Beckman IR-2

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[21] Stull, loc. cit.

[22] Melpolder, Woodbridge and Headington, loc. cit.

Table 3. Fractionation of Product from Run 3

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
1	-54	5.0	1.52	
2	54-58.5	"	2.54	
3	58.5-59.5	"	3.39	
4	59.5-60.0	"	4.73	
5	59.5-60.0	"	5.67	
6	60.0-60.5	"	6.53	
7	60.5-61.8	"	8.24	
8	61.8-62.0	"	9.41	1.4856
9	62.0-62.6	"	11.22	1.4864
10	62.6-63.0	"	12.83	1.4869
11	63.0-63.5	"	14.85	1.4873
12	63.5-63.9	"	16.92	1.4877
13	63.9-64.5	"	19.14	1.4877
14	64.5-65.0	"	20.86	1.4879
15	65.0-66.0	"	23.11	1.4881
16	65.5-66.5	"	26.07	1.4885
17	66.5-67.0	"	28.86	1.4890
18	67.0-67.0	"	31.71	1.4891
19	67.0-67.5	"	32.21	1.4893
20	67.5-105.0	"	33.59	1.4951
21	105.0-111.0	"	35.24	1.5070
22	111.0-111.8	"	36.62	1.5108
23	111.8-112.0	"	37.51	1.5110
24	112.0-112.0	"	39.10	1.5116
25	112.0-112.5	"	43.80	1.5118
26	112.5-112.8	"	45.48	1.5117
27	112.8-112.8	"	48.07	1.5118
28	112.8-113.0	"	49.01	1.5120
29	113.0-113.5	"	51.18	1.5120
30	113.2-113.2	"	52.55	1.5120
31	112.0-112.5	"	53.93	1.5125
32	112.5-112.9	"	55.08	1.5129
33	112.9-113.0	"	55.98	1.5128
34	113.0-113.0	"	57.28	1.5125
35	112.0-112.0	"	59.11	1.5125
36	112.0-112.0	"	60.91	1.5123
37	112.0-112.2	"	74.65	1.5123
38	111.0-111.7	4.5	76.79	1.5129

Table 3. Continued

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
39	111.7-112.0	4.5	80.37	1.5126
40	112.0-112.2	"	86.06	1.5125
41	112.0-112.2	"	90.22	1.5125
42				
43	114.5-115.9	4.7	91.42	1.5140
44	115.9-117.0	5.0	92.44	1.5134
45	117.0-117.5	"	93.21	1.5130
46	117.5-117.6	"	94.22	1.5130
47	117.6-117.7	"	95.10	1.5126
48	117.7-117.5	"	96.56	1.5126
49	117.5-118.0	"	98.96	1.5123
50	118.0-119.0	"	99.94	1.5121
51	119.0-119.7	"	101.45	1.5121
52	119.5-119.6	"	104.47	1.5123
53	119.6-119.6	"	105.82	1.5120
54	117.5-117.6	4.5	107.11	1.5120
55	117.6-117.7	"	108.57	1.5120
56	117.7-117.8	"	112.72	1.5120
57	117.9-118.0	"	115.12	1.5120
58	118.0-118.0	"	120.11	1.5129
59	118.0-117.8	"	124.31	1.5129
60	117.8-117.0	"	128.29	1.5127
61		"	132.82	1.5129
62		"	134.66	1.5126
63		"	140.85	1.5135

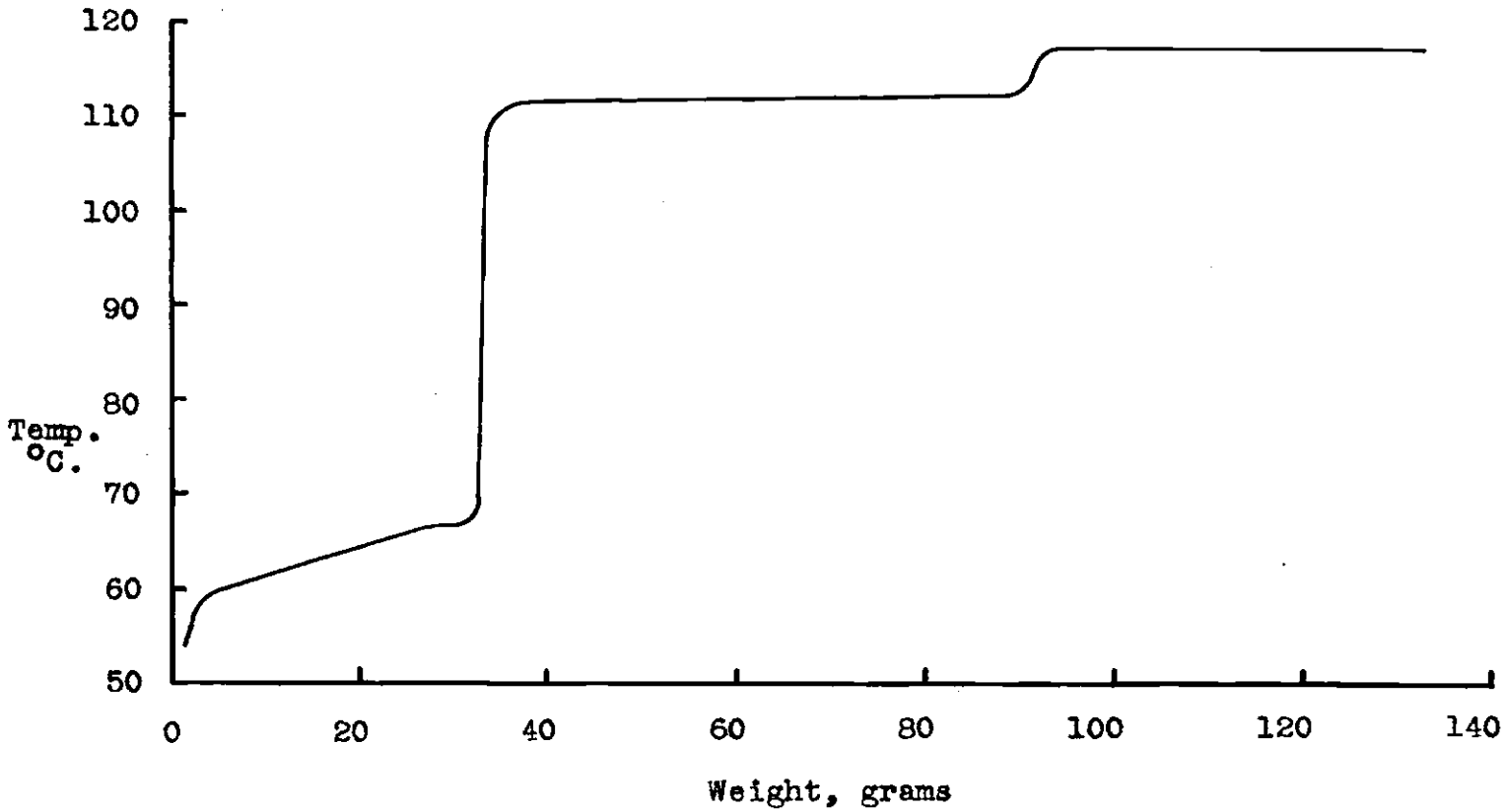

Figure 3. Run 3 Rectification Curve

infrared spectrometer. The absorptions at 12.03, 12.58, and 13.1 microns are characteristic of 1,4- 1,3- and 1,2-di-iso-propyl-benzene, respectively.[22]

To verify further the presence of isomeric di-iso-propyl-benzenes, the effect of anhydrous aluminum chloride on cumene under the conditions of the reaction was investigated. In a 500 ml. flask, 14.2 g. (0.1 mole) of aluminum chloride and 117.8 g. (0.98 mole) of cumene were stirred for four hours at a temperature of 5-10°C. The reaction mixture was poured onto 30 ml. of water and 70 g. of ice with vigorous stirring. The two layers were separated and the organic layer washed with two 25 ml. portions of a 5 per cent sodium carbonate solution then with four 10 ml. portions of water. The organic layer was dried with anhydrous sodium sulfate over night. The infrared spectra of the cumene before and after treatment with aluminum chloride was run from 10.0 to 14.5 microns wavelength. The absorptions at 12.02 and 12.58 microns that were shown by the cumene after treatment with aluminum chloride and not before, are characteristic of 1,4- and 1,3-di-iso-propyl-benzene, respectively.[23] This fairly well establishes that isomeric di-iso-propyl-benzenes were produced during the reaction of cumene and propylene oxide and were present in fractions 2 through 19 from Run 3.

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[23]Melpolder, Woodbridge and Headington, loc. cit.

Run 4.--The same general procedure and the same amounts of chemicals were used in this run as in Run 1. The temperature of the reaction was maintained at or below 5°C. during the addition of the contents of the dropping funnel, which required three hours four minutes. Stirring was continued for an additional thirty minutes. After the separation of the two layers, the water layer was extracted with 20 ml. of cumene. The organic layer, along with the cumene extract, was washed and dried in the same manner as in Run 2. The sodium sulfate was filtered from the solution of the product and the excess cumene was distilled off at a pressure of 110 mm. of mercury. The remaining product was fractionated at a pressure of 5 mm. into 37 fractions, Table 4. The rectification curve, Figure 4, indicated two main products from the fractionation. The total yield of product, based on one mole of propylene oxide, was 63.4 per cent of theory. The yield of the lower boiling material, calculated from the rectification curve, was 54 per cent of the total yield.

Run 5.--The same general procedure and the same amounts of chemicals were used in this run as in Run 1. The addition of the contents of the dropping funnel required one hour forty-five minutes during which the temperature remained between 4 and 6°C. The stirring was continued for thirty minutes after the addition was complete. The organic layer

Table 4. Fractionation of Product from Run 4

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
1	-67	5.0	2.50	
2	67-110	"	4.81	
3	110-112	"	5.63	
4	111.2-112.0	"	6.56	
5	112.0-112.1	"	7.62	
6	112.1-112.2	"	8.56	1.5113
7	112.2-112.5	"	9.86	1.5116
8	112.5-112.7	"	10.89	1.5115
9	113.0-113.2	"	12.48	1.5115
10	112.6-112.8	"	14.24	1.5119
11	112.8-112.9	"	17.03	1.5126
12	112.8-113.0	"	19.02	1.5125
13	112.6-113.0	"	26.43	1.5130
14	113.0-113.0	"	33.95	1.5130
15	113.0-113.2	"	42.81	1.5131
16	113.2-113.3	"	44.05	1.5125
17	113.3-113.3	"	47.14	1.5128
18	113.3-113.3	"	53.63	1.5130
19	113.3-113.5	"	57.36	1.5134
20	113.5-113.9	"	60.14	1.5131
21	113.9-114.4	"	63.50	1.5132
22	114.2-114.6	"	65.37	1.5129
23	114.6-115.0	"	66.95	1.5130
24	115.0-116.0	"	68.53	1.5130
25	116.0-116.9	"	70.35	1.5130
26	116.9-117.1	"	71.95	
27	117.1-117.1	"	73.25	
28	117.1-117.3	"	74.63	
29	117.3-117.5	"	76.50	
30	117.5-117.9	"	78.64	
31	117.9-117.9	"	86.27	
32	119.0-119.0	"	93.21	
33	119.0-119.0	"	100.12	
34	119.5-119.5	"	107.68	
35	119.5-119.5	"	114.20	
36		"	117.84	
37		"	118.61	

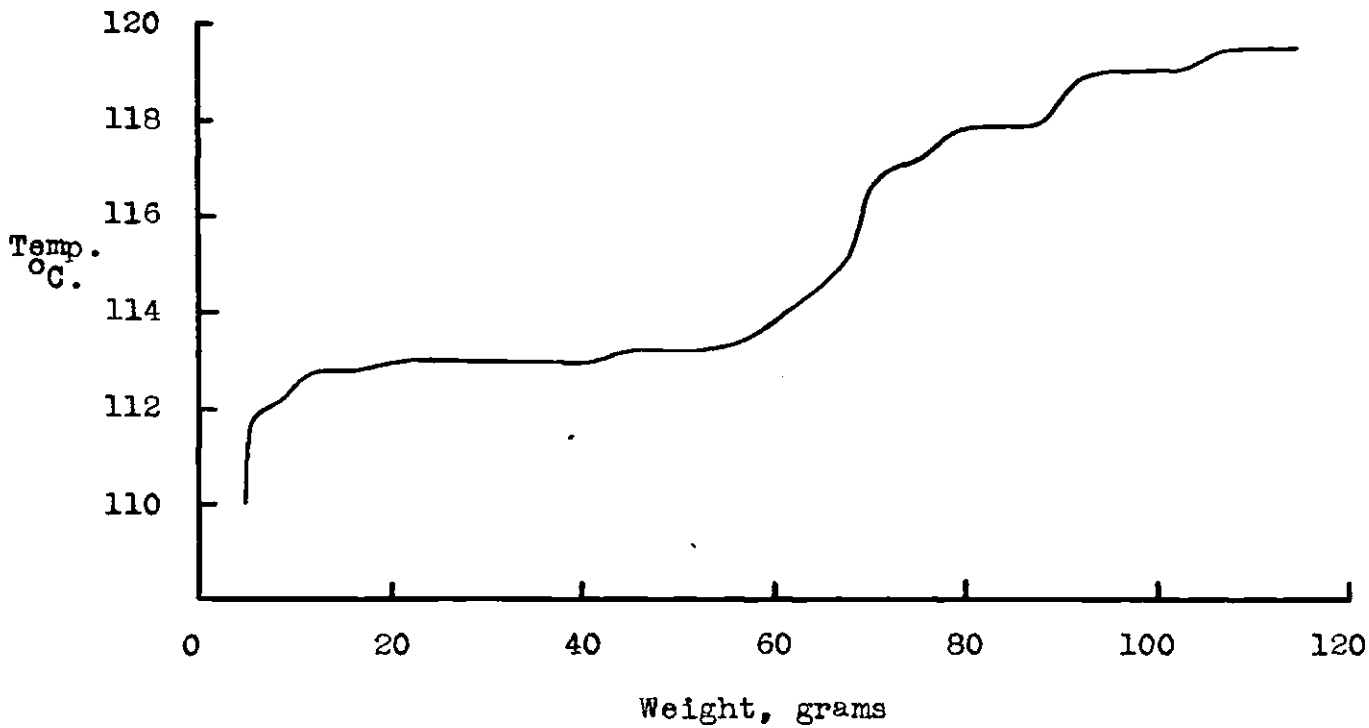

Figure 4. Run 4 Rectification Curve

was washed and dried in the same manner as in Run 2. The excess cumene was distilled off at a pressure of 110 mm. of mercury after the sodium sulfate had been removed by filtration. The remaining product was fractionated at a pressure of 5 mm. into 33 fractions, Table 5. The rectification curve, Figure 5, indicated two main products. The total yield of product, based on one mole of propylene oxide, was 64.6 per cent of theory. The yield of the lower boiling material was 53 per cent of the total yield.

Table 5. Fractionation of Product from Run 5

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
1	-108	5.0	4.66	1.4883
2	105.2-112.9	"	5.09	1.5020
3	112.9-113.2	"	5.84	1.5100
4	113.2-113.1	"	6.53	1.5115
5	110.9-111.3	"	7.26	1.5116
6	111.3-111.7	"	7.93	1.5120
7	111.7-111.9	"	9.01	1.5120
8	111.4-111.6	"	10.43	1.5121
9	111.9-112.0	"	17.34	1.5122
10	112.0-112.0	"	24.21	1.5128
11	112.0-112.0	"	31.48	1.5129
12	112.0-112.0	"	38.40	1.5131
13	112.0-112.0	"	44.82	1.5131
14	112.0-112.2	"	51.57	1.5131
15	112.2-112.7	"	53.78	1.5132
16	112.7-113.0	"	56.22	1.5133
17	113.0-113.2	"	60.04	1.5133
18	113.2-113.5	"	61.49	1.5131
19	113.5-114.0	"	64.75	1.5132
20	114.0-114.7	"	66.92	1.5130
21	114.7-115.0	"	68.93	1.5130
22	115.0-115.0	"	71.27	1.5130
23	115.0-115.6	"	73.04	1.5130
24	115.6-116.0	"	75.47	1.5130
25	115.9-116.1	"	78.03	1.5130
26	116.1-116.2	"	80.34	1.5130
27	116.2-116.5	"	82.12	1.5130
28	116.5-116.7	"	90.04	1.5129
29	116.7-116.7	"	97.10	
30	116.7-116.7	"	104.99	
31	116.7-116.0	"	111.01	
32			118.50	
33			120.18	

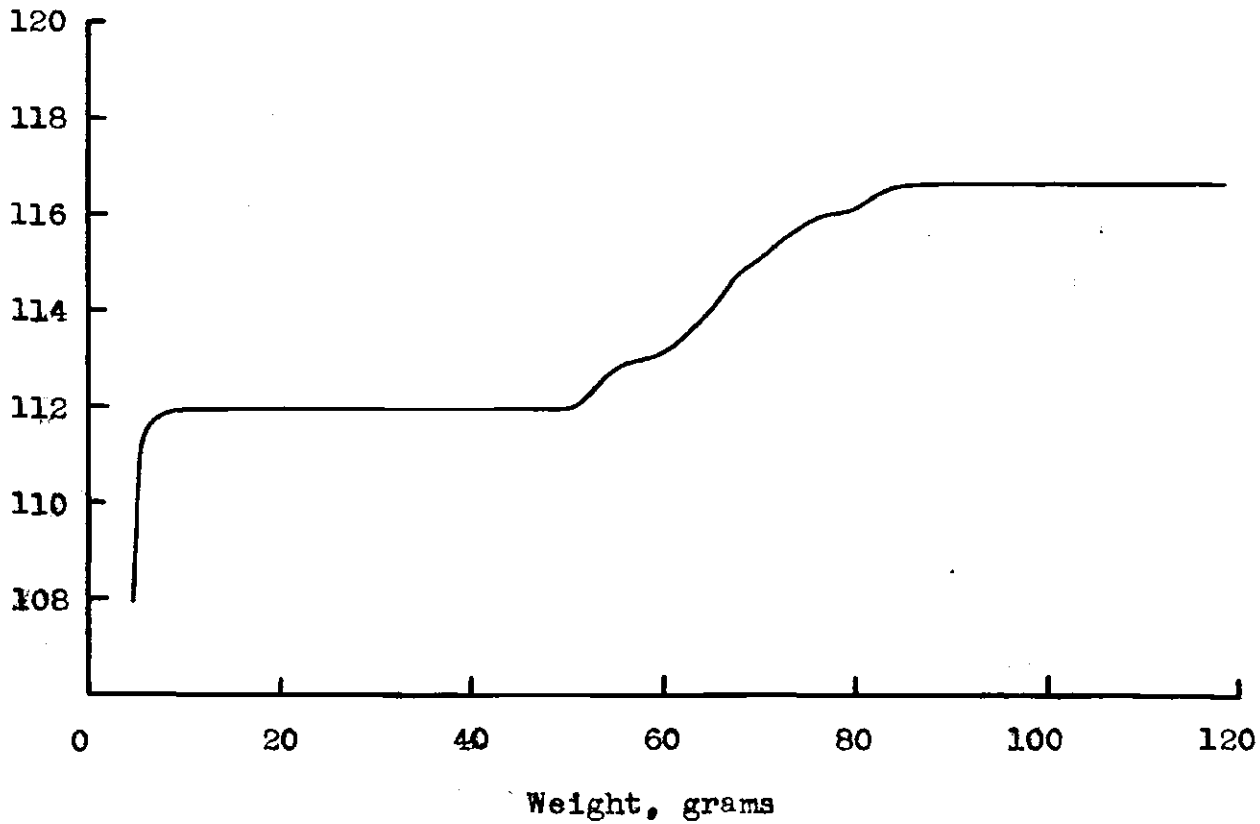

Figure 5. Run 5 Rectification Curve

IDENTIFICATION OF PRODUCTS

Evidence is presented in this section to show that the products from the reaction of cumene with propylene oxide were alcohols, therefore they will be called the higher boiling and lower boiling alcohols throughout the section.

Higher Boiling Alcohol.--After several attempts to oxidize the alcohols to dibasic acids with basic permanganate, acid dichromate, chromium trioxide in glacial acetic acid, and dilute nitric acid, it was found that the dilute nitric acid yielded the best results. The higher boiling alcohol was oxidized to the dibasic acid in the following way. A mixture of 10 ml. of fractions 22 and 23 from Run 1, 70 ml. of water and 60 ml. of concentrated nitric acid was refluxed for 28 hours, at the end of which no oil remained in the flask. The reaction mixture was cooled in iced water, filtered, and the solid washed with cold water. The solid was boiled with 100 ml. of water, cooled, and filtered. After drying, the solid was extracted with benzene in a Soxhlet extractor for one hour. The solid remaining in the extractor had a melting point of 180-200°C. The methyl ester of the acid was prepared by heating 0.2 g. of the acid with 0.5 g. of phosphorus pentachloride in a dry test

tube until a clear liquid was produced, then adding 10 ml. of absolute methanol to the cooled liquid. After the reaction was complete the solution was poured into 10 ml. of water. The white precipitate was removed by filtration and recrystallized from a mixture of one ml. of water and four ml. of methanol. The flaky white crystals had a melting point of 136-140°C. After recrystallization from absolute methanol, the methyl ester melted at 139.0-140.5°C. The reported melting point of the methyl ester of terephthalic acid is 140°C.[24] Therefore, the higher boiling alcohol must be the *para* isomer.

The O-alkylsaccharin derivative of the higher boiling alcohol (fraction 30, Run 5) was prepared by the method reported by Meadoe and Reid.[25] After five recrystallizations from ethanol the derivative had a melting point of 164.8-167.0°C.

The wide melting range of the derivative indicated that the higher boiling alcohol was impure. Therefore, as indicated by the rectification curves, certain fractions were combined and refractionated. The fractions combined and fractionation data are given in Table 6. The refractive indices given are for the fractions that were collected as

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[24] S. P. Mullikin, "*Identification of Pure Organic Compounds*," John Wiley and Sons, Inc., New York, N. Y., 1904, Vol. I, p. 85.

[25] J. R. Meadoe and E. E. Reid, *J. Am. Chem. Soc.*, *65*, 457 (1943).

Table 6. Refractionation of Higher Boiling Alcohol

Charge: Fraction Nos. 20-21 from Run 2
Fraction Nos. 46-61 from Run 3
Fraction Nos. 26-36 from Run 4
Fraction Nos. 29-32 from Run 5

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
1	-98.4	3	1.55	1.5130
2	98.4-100.7	"	3.00	1.5130
3	100.7-101.2	"	4.34	1.5130
4	101.2-103.4	"	6.16	1.5130
5	103.4-103.8	"	7.29	1.5129
6	103.8-103.8	"	8.76	1.5128
7	103.8-103.6	"	9.95	1.5125
8	103.6-103.8	"	11.02	1.5122
9	103.7-103.8	"	12.48	1.5129
10	103.8-104.0	"	13.98	1.5128
11	104.0-103.8	"	15.43	1.5127
12	103.7-103.9	"	17.16	1.5127
13	103.9-103.8	"	19.51	1.5128
14	103.8-103.6	"	21.51	1.5126
15	103.7-103.7	"	24.32	1.5126
16	103.8-103.8	"	28.09	1.5129
17	103.8-103.7	"	32.48	1.5130
18	103.7-103.4	"	36.27	
19	103.4-103.4	"	42.19	
20	103.4-103.2	"	46.96	
21	103.2-103.2	"	53.55	
22	103.2-103.2	"	58.01	1.5130
23	103.5-103.2	"	63.16	1.5129
24	103.2-103.2	"	67.13	1.5129
25	103.3-103.4	"	72.96	
26	103.4-103.4	"	77.91	
27	103.4-103.2	"	84.19	
28	103.2-103.3	"	90.12	
29	103.2-103.3	"	95.61	

Table 6. Continued

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
30	103.2-103.2	3	100.85	
31	103.2-103.4	"	107.65	
32	103.2-103.4	"	113.61	
33	103.4-103.2	"	120.32	
34	103.4-104.3	"	126.50	
35	104.8-104.9	"	129.56	
36	105.2-105.2	"	132.15	

liquids; all other fractions were obtained as solids. A heat lamp was used to melt the solid as it collected in the take-off assembly from fractions 16 through the remainder of the fractionation.

The O-alkylsaccharin derivative of fraction 19 of the refractionated higher boiling alcohol melted from 166.5-168.2°C. after four recrystallizations.

The wide melting range of the derivative indicated that the refractionated higher boiling alcohol was impure. This was further indicated by the melting points of fractions of the redistilled alcohol. Fraction 10 melted from 42.5-44.0°C. Fraction 25 melted from 43.5-44.5°C. and fraction 34 melted from 44.0-45.5°C. No further attempts were made to purify the higher boiling alcohol.

Several attempts were made to prepare the p-nitrophenyl-urethan and the alpha-naphthylurethan of the alcohol but a solid derivative could not be obtained.

Lower Boiling Alcohol.--A representative sample of the lower boiling alcohol was oxidized to the dibasic acid with dilute nitric acid. Into a 300 ml. flask equipped with a reflux condenser was added 10 ml. of fractions 17 and 18 from Run 1, 100 ml. of water, and 25 ml. of concentrated nitric acid. The mixture was refluxed 54 hours during which 40 ml. of concentrated nitric acid was added. The mixture was cooled and filtered. The solid collected was boiled with

50 ml. of water, cooled, filtered, and dried. The light yellow solid was extracted with benzene in a Soxhlet extractor for about five hours then removed and dried. The light yellow solid had a melting point of 338-344°C. The reported melting point of isophthalic acid is 345-347°C.[26] The methyl ester was prepared by heating 0.2 g. of the acid with 0.5 g. of phosphorus pentachloride in a dry test tube until a clear liquid was obtained, then adding two ml. of absolute methanol to the cooled liquid. After the reaction was complete, the solution was poured into five ml. of cold water. The white precipitate was filtered from the solution and dried. It melted from 58-61°C. After recrystallization from a one to one mixture of ethanol and water the methyl ester had a melting point of 64-64.5°C. The reported melting point of the methyl ester of isophthalic acid is 64°C.[27] This indicated that the lower boiling alcohol was the meta isomer.

The O-alkylsaccharin derivative of the lower boiling alcohol was prepared from combined fractions 17 and 18 from Run 1. After five recrystallizations from ethanol the derivative melted from 110-140°C.

The wide melting range of the derivative indicated that the lower boiling alcohol probably was a mixture of

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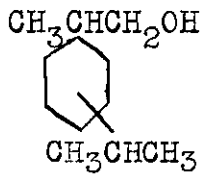
[26]Beilstein, "Handbuch der organischen Chemie," Julius Springer, Berlin, 4th ed., Vol. IX, 1926, p. 833.

[27]Mullikin, loc. cit.

alcohols. Therefore, as shown by the rectification curves, certain lower boiling alcohol fractions were combined and refractionated. The fractions combined and the fractionation data are given in Table 7. The refractive indices of the fractions from the refractionation clearly show that the lower boiling alcohol was a mixture of compounds inseparable by this type of distillation. No further attempts were made to purify the lower boiling alcohol.

The density of combined fractions 23 through 27, Table 7, of the lower boiling alcohol was determined with a two ml. pycnometer calibrated with mercury and distilled water at 25°C. with reference to water as 1.00000 g. per ml. at 4°C. The average density from three determinations was 0.9583 g. per ml. at 25°C. The experimental molar refraction[28] was found to agree with the molar refraction calculated from atomic refractions[28] for a compound having the formula--



Refractive index at 25°C. = 1.5135
Density at 25°C. = 0.9583
Experimental molar refraction = 55.96
Calculated molar refraction = 55.54.

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[28]Landolt-Bornstein, Physikalisch-Chemische Tabellen, Vol. 2, (1923), p. 985.

Table 7. Refractionation of Lower Boiling Alcohol

Charge: Fraction Nos. 25-41 from Run 3
Fraction Nos. 13-18 from Run 4
Fraction Nos. 10-14 from Run 5

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
1	-99.1	3	0.07	1.5103
2	98.3-99.4	"	0.44	1.5099
3	100.0-101.2	"	0.75	1.5080
4	101.4-101.6	"	1.52	1.5088
5	101.6-101.8	"	1.89	1.5090
6	101.8-102.0	"	2.75	1.5100
7	102.0-102.2	"	3.49	1.5100
8	102.2-102.4	"	4.65	1.5105
9	102.4-102.4	"	6.37	1.5112
10	102.5-102.5	"	6.81	1.5110
11	101.7-101.7	"	7.58	1.5110
12	101.6-101.8	"	7.97	1.5110
13	101.8-101.8	"	11.18	1.5119
14	101.8-101.8	"	13.77	1.5121
15	101.6-101.6	"	18.13	1.5123
16	"	"	22.22	1.5126
17	"	"	27.60	1.5130
18	"	"	31.60	1.5130
19	"	"	37.97	1.5130
20	"	"	44.32	1.5131
21	"	"	50.76	1.5132
22	"	"	57.57	1.5133
23	"	"	64.60	1.5135
24	"	"	67.70	1.5135
25	"	"	72.55	1.5133
26	"	"	78.06	1.5135
27	"	"	85.11	1.5136
28	"	"	91.42	1.5139
29	101.5-101.6	"	98.67	1.5145
30	101.6-101.6	"	102.34	1.5149
31	101.6-105.0	"	107.36	1.5130
32	105-	"	110.99	1.5128

The O-alkylsaccharin derivative of combined fractions 23 through 27, Table 7, of the lower boiling alcohol was prepared. After ten fractional recrystallizations from a one to one mixture of ethanol and ethyl acetate, a portion of the derivative melted from 183.5-184.0°C. A more soluble fraction of the derivative melted from 107-115°C.

The preparation of the derivative yielded two compounds that were partially separable by fractional recrystallization, therefore it was concluded that the lower boiling alcohol was a mixture of alcohols and not a single alcohol contaminated with high boiling hydrocarbons. Since it had been found that the lower boiling alcohol contained a meta isomer it was thought that an ortho isomer was also present. However, ortho-phthalic acid could not be identified in the nitric acid oxidation products of several fractions of the lower boiling alcohol. The inability to identify ortho-phthalic acid is not too surprising in view of the fact that a compound having a similar structure, 1,2-di-isopropyl-benzene, has been found resistant to oxidation with chromic acid and permanganate solutions at 100°C.[29]

Preparation of the 3,5-dinitrobenzoate, p-toluene sulfonate, 3-nitrophthalate, p-nitrophenylurethan, and alpha-naphthylurethan derivatives of the lower boiling alcohol was attempted. However, a solid derivative was not obtained in any of the attempts.

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[29]Melpolder, Woodbridge and Headington, op.cit., p.938.

CONVERSION OF ALCOHOLS TO ALDEHYDES

Although it was known that the alcohols were not pure compounds, they were oxidized to the aldehydes. The aldehydes were prepared to determine whether they could be obtained as pure compounds and to also investigate their odor value.

A method of oxidizing primary alcohols to aldehydes has been reported by Oppenauer and Oberrauch.[30] They obtained good yields of benzaldehyde by the oxidation of benzyl alcohol with di-t-butyl chromate. Leo and Westheimer have studied this reaction and found that pyridine exhibited a positive catalytic effect upon the oxidation.[31] The oxidization of benzyl alcohol, as modified by Westheimer, was repeated to become acquainted with the reaction and an 83 per cent yield of benzaldehyde was obtained.

The alcohols, prepared by the reaction of cumene with propylene oxide, were oxidized to the corresponding aldehydes with di-t-butyl chromate as follows. The di-t-butyl chromate oxidizing agent was prepared by slowly adding 20 g. (0.20 moles) of chromium trioxide to a solution of

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[30] R. Oppenauer and H. Oberrauch, Anales. Asoc. quim argentina, 37, 276 (1949).

[31] A. Leo and F. H. Westheimer, J. Am. Chem. Soc., 74, 4383 (1952).

44.4 g. (0.60 mole) of t-butyl alcohol in 70 ml. of benzene. The temperature of the t-butyl alcohol solution was maintained at or below 10°C. by an ice bath during the addition of the chromium trioxide. At higher temperatures rapid decomposition occurred in the solution. After all the chromium trioxide had dissolved, the bright red solution was dried with anhydrous sodium sulfate. In all oxidizations the di-t-butyl chromate solution was used within one hour after its preparation. Into a one liter three-necked flask, equipped with a stirrer, thermometer, and dropping funnel, was added 90 ml. of benzene, one ml. of pyridine and 26.7 g. (0.15 mole) of the alcohol to be oxidized. The flask was placed in an ice bath and the solution was allowed to cool. The sodium sulfate was filtered from the di-t-butyl chromate solution and washed with two 10 ml. portions of benzene. The oxidizing solution was slowly added to the alcohol solution in the flask during a period of 20 minutes by means of the dropping funnel, with the temperature of the reaction remaining between 5 and 7°C. Stirring was continued for an additional 25 minutes, then the reaction was stopped by the addition of about one g. of oxalic acid followed by the addition of 50 ml. of water at such a rate to keep the temperature below 15°C. Thirty-nine g. of oxalic acid was slowly added over a period of about 10 minutes with the temperature around 15°C. Gas was evolved

during the addition of the oxalic acid. Two hundred fifty ml. of 20 per cent sulfuric acid was added over a period of 30 minutes at such a rate to keep the temperature from 12-16°C. The ice bath was removed and heating of the flask was begun by means of a heating mantle. After heating the reaction mixture for about one hour at 40-50°C., steam distillation of the product was begun and continued for three hours. The two layers were separated after thorough shaking in a separatory funnel. The water layer was extracted twice with 50 ml. portions of benzene and the extracts were added to the organic layer. The organic layer was extracted twice with 25 ml. portions of 5 per cent sodium carbonate solution to remove the acid formed in the oxidation. The organic layer was washed with four 15 ml. portions of water and placed over anhydrous sodium sulfate to dry over night. The drying agent was filtered from the solution of the aldehyde and washed with 10 ml. of benzene. The benzene was distilled off at atmospheric pressure and the remaining product was fractionated under vacuum in a Todd column,[32] packed with a Monel spiral.

The product obtained from the oxidation of the higher boiling alcohol, combined fractions 20 and 21 from Run 1 and fractions 22 and 23 from Run 2, was fractionated at a pressure of about 3 mm. of mercury. The yield of

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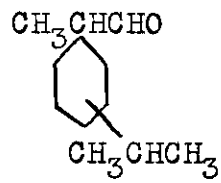
[32] F. Todd, loc. cit.

aldehyde which boiled at 96-102°C. was 18.15 g. or 68.8 per cent of theory. The three aldehyde fractions were combined and refractionated at a pressure of 5 mm. of mercury. The fractionation data are given in Table 8. The density of fraction 4, from three determinations, was 0.9569 g. per ml. at 25°C. The experimental molar refraction agreed with the calculated molar refraction of an aldehyde having the formula--



Refractive index at 25°C. = 1.5101
Density at 25°C. = 0.9569
Experimental molar refraction = 55.10
Calculated molar refraction = 55.03.

The product obtained from the oxidation of the refractionated higher boiling alcohol, combined fractions 19 through 24, Table 6, was distilled at a pressure of 2.5 mm. of mercury. The distillation data are given in Table 9. The yield from the oxidation was 53.4 per cent of theory. The density of fraction 5, from two determinations, was 0.9558 g. per ml. at 25°C. The experimental molar refraction agreed with that of the previously prepared aldehyde, described above.

Refractive index at 25°C. = 1.5098
Density at 25°C. = 0.9558
Experimental molar refraction = 55.11
Calculated molar refraction = 55.03.

Table 8. Fractionation of Aldehyde from Higher Boiling Alcohol

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
1	100.0-101.0	5	0.68	1.5094
2	101.0-101.1	"	1.58	1.5100
3	101.1-101.1	"	5.34	1.5100
4	101.1-101.4	"	8.28	1.5101
5	101.4-102.0	"	11.18	1.5102
6	101.6-	"	13.55	1.5110
7		"	13.99	1.5120

Table 9. Fractionation of Aldehyde from Refractionated Higher Boiling Alcohol

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
1	83.6-83.6	2.5	0.30	1.5145
2	83.6-83.7	"	1.58	1.5101
3	84.8-84.8	"	2.82	1.5103
4	84.8-84.8	"	6.22	1.5098
5	84.8-85.0	"	11.60	1.5098
6	85.0-85.0	"	14.12	1.5110

The aldehyde is a rather viscous, clear liquid with an odor definitely of the wood type. The odor is imitative of ionone although sweeter and minty. An absorbent paper lost most of its odor within a week after being dipped in the aldehyde.

The 2,4-dinitrophenylhydrazone of the aldehyde, fraction 4, Table 8, was prepared by the usual procedure.[33] The derivative melted from 105-121°C. after one recrystallization from dilute ethanol. After the second recrystallization, the derivative melted from 116-126°C. Since it has been shown that some 2,4-dinitrophenylhydrazones do not have sharp melting points,[34] the semicarbazone of a sample of the aldehyde, fraction 4, Table 8, was prepared by the usual method.[35] After four recrystallizations from dilute ethanol, the semicarbazone melted from 141-152°C.

The wide melting ranges of the two aldehyde derivatives indicated that the product from the oxidation of the higher boiling alcohol is a mixture of aldehydes.

An acid was also produced during the oxidation of the higher boiling alcohol. The base extract of the organic layer from the steam distillation of the second

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[33]R. L. Shriner and R. C. Ruson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 3rd Ed., 1948, p. 171.

[34]L. I. Braddock, et.al., Anal. Chem., 25, 301 (1953).

[35]Shriner and Fuson, op. cit., p. 170.

aldehyde preparation, described above, was acidified with dilute sulfuric acid. The precipitated solid acid was filtered from the acidic solution and dried. The acid melted from 64-68°C. The 1.4 g. of acid was dissolved in a minimum amount of 5 per cent sodium hydroxide solution at a temperature of 50°C. When the solution was allowed to cool, a white, flaky solid began to crystallize so the solution was cooled in ice water to crystallize more of the material. The solid was filtered from the solution and dried. The solid, believed to be the sodium salt of the acid, had a melting point of 109-118°C. A solution of the salt in 50 ml. of water was acidified with 10 per cent sulfuric acid, filtered, and the solid collected was dried. The acid melted from 60-70°C. After three recrystallizations from an acetone and water solution, the acid melted from 68-73°C. After drying for several hours in a vacuum desiccator the acid melted from 71-74°C. The neutralization equivalent of the acid was determined by dissolving a known weight of the acid in 75 ml. of ethanol and titrating the solution with a standard sodium hydroxide solution. The average neutralization equivalent from two determinations was 194. This agrees with the molecular weight of a monobasic acid having the empirical formula $C_{12}H_{16}O_2$ and molecular weight of 192.

A sample of the aldehyde was oxidized to the corresponding acid in order to determine the molecular weight of

the aldehyde. One g. of the aldehyde, fraction 4, Table 9, in 10 ml. of a very dilute sodium hydroxide solution was shaken with added portions of a saturated solution of potassium permanganate until no more permanganate was discolored. Just enough ethanol was added to the solution to discolor the excess permanganate and the solution was filtered several times to remove the manganese dioxide. Upon acidification of the solution an oil separated which soon crystallized. The white solid acid was recrystallized from an acetone-water solution and dried. It melted from 71-73.5°C. The neutralization equivalent of the acid was found to be 194 by titrating a known weight of the acid in 75 ml. of ethanol with a standard sodium hydroxide solution. This neutralization equivalent is the same as that of the acid obtained from the preparation of the aldehyde, described above. Therefore, the aldehyde must have the empirical formula $C_{12}H_{16}O$.

The product obtained from the oxidation of the refractionated lower boiling alcohol, fractions 18 through 22, Table 7, was fractionated at a pressure of 3.5 mm. of mercury. The fractionation data are given in Table 10. The yield from the oxidation was 51.1 per cent of theory. The density, from two determinations, of combined fractions 9 and 10 of the aldehyde was 0.9609 g. per ml. at 25°C. The experimental molar refraction of the aldehyde agreed with

the calculated molar refraction of an aldehyde having the formula given on page 37:

Refractive index at 25°C. = 1.5076
Density at 25°C. = 0.9609
Experimental molar refraction = 54.64
Calculated molar refraction = 55.03.

The aldehyde is a rather viscous, clear liquid with an odor definitely of the precious wood type. An absorbent paper, previously dipped in the aldehyde, had a pronounced cedar wood odor after standing in air for about a week.

The alkaline extract of the product from the oxidation of the lower boiling alcohol was acidified with dilute sulfuric acid. The oil which immediately separated would not solidify when cooled in an ice bath. Recrystallization of the oil failed to yield a solid.

One g. of the aldehyde, fraction 13, Table 10, was oxidized to the acid by the method described above. Upon acidification of the basic solution from the oxidation an oil separated. The oil would not solidify when cooled in an ice bath. The fact that the acid was obtained as an oil is in agreement with the acid obtained from the preparation of the aldehyde as described in the previous paragraph.

Table 10. Fractionation of Aldehyde from Lower Boiling Alcohol

Fraction No.	Temperature °C.	Pressure mm. Hg.	Total Wt. g.	n_D^{25}
1	-86.5	3.5	0.63	1.5096
2	86.5-86.9	"	1.51	1.5085
3	86.9-87.2	"	2.40	1.5080
4	87.2-87.3	"	3.23	1.5078
5	87.3-87.3	"	4.16	1.5077
6	87.2-87.2	"	5.05	1.5076
7	87.2-87.2	"	5.86	1.5076
8	87.2-87.3	"	6.73	1.5075
9	87.2-87.1	"	8.02	1.5076
10	87.1-87.1	"	9.83	1.5077
11	87.2-87.2	"	11.22	1.5076
12	87.2-87.3	"	12.15	1.5078
13	87.2-87.3	"	13.30	1.5079
14	87.4-87.3	"	14.11	1.5081

CONVERSION OF ALCOHOLS TO OLEFINS

The dehydration of the alcohols, prepared by the reaction of cumene with propylene oxide, was attempted to determine whether they were of the phenethyl type and to compare the physical properties of the products with known compounds.

Sabetay found that primary alcohols of the phenethyl type were nearly quantitatively converted to the corresponding styrenes by heating with solid potassium hydroxide.[36] In a mixture of hydratropic alcohol and methylbenzyl carbinol, only the hydratropic alcohol was dehydrated.[37] An unsuccessful attempt to dehydrate cyclohexyl ethanol indicated the necessity of having an aromatic ring or unsaturated group attached to the ethanol group.[38]

The alcohols were dehydrated as follows. Into a 50 ml. distilling flask was placed 10 g. of the alcohol to be dehydrated and 6 g. of potassium hydroxide pellets. The flask was heated with a low flame, and two phases were formed in about 15 minutes. Heating was increased and the product was distilled. The product was extracted with

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[36] S. Sabetay, Bull. soc. chim. France, 45, 69 (1929).

[37] S. Sabetay, Bull. soc. chim. France, 47, 614 (1930).

[38] S. Sabetay and T. Mintsou, Bull. soc. chim. France, 45, 842 (1929).

20 ml. of diethyl ether, and the ether solution was washed twice with 4 ml. portions of water. After drying the solution with anhydrous sodium sulfate, the ether was evaporated by vacuum and the product was fractionated with a column 45 cm. long and 5 mm. in diameter packed with a spiral tantalum wire. All the olefin fractionations were carried out at atmospheric pressure.

The olefin obtained from the dehydration of a representative sample of the higher boiling alcohol, fractions 16, 17, and 18, Table 6, was fractionated into 6 fractions, Table 11. Combined fractions 4,5, and 6 had a density of 0.8855 at 25°C. Fractions 2 through 6 were combined and redistilled at atmospheric pressure. The distillation, Table 12, yielded six fractions boiling from 218.2-221.1°C. The refractive indices of consecutive fractions varied considerably, so more of the olefin was prepared in order to have enough for a more accurate fractionation. The olefin obtained from the dehydration of a representative sample of the higher boiling alcohol, fractions 14 and 15, Table 6, was fractionated at atmospheric pressure, Table 13. Combined fractions 4,5, and 6 had a density of 0.8847 at 25°C. Fractions 3, 4, 5, and 6, Table 13, were combined with fractions 3, 4, 5, and 6, Table 12, of the previously prepared olefin, and refractionated, Table 14. Combined fractions 5 and 6 had a density of 0.8851 at 25°C.

Table 11. Fractionation of Olefin from Higher Boiling Alcohol

Fraction No.	Temperature °C.	Total Wt. g.	n_D^{25}
1	213.2-218.6	0.16	1.5122
2	218.6-220.2	0.51	1.5192
3	220.2-220.4	1.15	1.5222
4	220.3-219.4	2.36	1.5226
5	220.2-220.2	3.14	1.5229
6		3.50	1.5229

Table 12. Refractionation of Olefin from Higher Boiling Alcohol

Fraction No.	Temperature °C.	Total Wt. g.	n_D^{25}
1	218.2-220.4	0.24	1.5180
2	220.4-220.8	0.39	1.5209
3	220.7-221.0	0.56	1.5219
4	221.0-221.1	1.33	1.5226
5	221.1-219.7	2.14	1.5229
6		2.62	1.5219

Table 13. Fractionation of Olefin from Higher Boiling Alcohol

Fraction No.	Temperature °C.	Total Wt. g.	n_D^{25}
1	217.2-219.8	0.24	1.5174
2	219.8-220.7	0.42	1.5210
3	220.7-221.0	0.76	1.5224
4	221.0-220.8	1.88	1.5229
5	220.8-219.0	2.51	1.5229
6		2.89	1.5228

Table 14. Refractionation of Olefin from Higher Boiling Alcohol

Fraction No.	Temperature °C.	Total Wt. g.	n_D^{25}
1	219.2-220.4	0.14	1.5195
2	220.3-220.6	0.34	1.5209
3	220.6-220.8	0.65	1.5219
4	220.8-220.8	1.01	1.5223
5	220.8-221.0	1.98	1.5228
6	221.0-219.8	3.37	1.5229
7		3.73	1.5227

The physical constants of the olefin prepared by the dehydration of the higher boiling alcohol agreed with the physical constants reported for 4-isopropyl-α-methyl styrene as follows.

	Boiling point °C.	Refractive index at 25°C.	Density
Found	220.8-221.0	1.5228	0.8851 at 25/4°C.
Reported[39]		1.5204	0.889 at 25/25°C.
Reported[40]	221.5 760 mm.	1.52155	0.88974 at 25/4°C.

The calculated molar refraction of 4-isopropyl-α-methyl styrene is 53.55. It is known that conjugated olefins such as styrene exhibit a positive optical exhaltation of about 1.76.[41] Therefore, by adding 1.76 to the calculated value, we obtain 55.31 as the correct calculated value. The experimental molar refraction of the olefin obtained from the dehydration of the higher boiling alcohol agreed with the calculated value for 4-isopropyl-α-methyl styrene as follows.

Refractive index at 25°C. = 1.5228
Density at 25°C. = 0.8851
Experimental molar refraction = 55.29
Calculated molar refraction = 55.31.

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[39]G. B. Bachman and H. M. Hellman, J. Am. Chem. Soc., 70, 1772 (1948).

[40]R. R. Dreisbach and R. A. Martin, Ind. Eng. Chem., 41, 2876 (1949).

[41]S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, 2nd ed., 1946, p. 530.

It has been reported that 2,4-dinitrobenzenesulfenyl chloride adds to many olefins to produce solid adducts with characteristic melting points.[42] The derivative of the higher boiling olefin was prepared from 0.4 g. of the 2,4-dinitrobenzenesulfenyl chloride in 5 ml. of glacial acetic acid. It was necessary to recrystallize the oil product several times from ethanol before the solid derivative was obtained. Seeding of the filtrates from the oil recrystallizations with the crystalline solid produced more crystals. The orange crystals were recrystallized from ethanol three times to a constant melting point of 75.5-77.0°C.

The olefin obtained from the dehydration of a representative sample of the lower boiling alcohol, fractions 23 through 27, Table 7, was fractionated at atmospheric pressure. The fractionation data are given in Table 15. A second dehydration of a sample of the lower boiling alcohol, fractions 23 through 27, Table 7, was run. The crude product was combined with fractions 3 through 7 from the previous dehydration and fractionated at atmospheric pressure. The fractionation data are given in Table 16. The density of combined fractions 4, 5, and 6 was 0.8838 g. per ml. at 25°C. The experimental molar refraction agreed with the calculated molar refraction of isopropyl-α-methyl styrene as follows.

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[42] N. Kharasch and C. M. Buess, J. Am. Chem. Soc., 71, 2724 (1949).

Table 15. Fractionation of Olefin from Lower Boiling Alcohol

Fraction No.	Temperature °C.	Total Wt. g.	n_D^{25}
1	196.5-203.2	0.09	1.5052
2	208.0-212.0	0.39	1.5138
3	212.2-213.1	0.65	1.5180
4	213.0-212.9	0.98	1.5191
5	212.9-213.5	1.34	1.5192
6	213.5-212.1	1.80	1.5195
7		2.16	1.5195

Table 16. Fractionation of Olefin from Lower Boiling Alcohol

Fraction No.	Temperature °C.	Total Wt. g.	n_D^{25}
1	200.4-212.2	0.55	1.5095
2	212.2-213.2	0.93	1.5178
3	213.2-213.6	1.46	1.5192
4	213.6-213.6	2.30	1.5195
5	213.6-213.7	3.13	1.5195
6	213.7-213.8	3.55	1.5196
7	213.7-236.4	4.05	1.5198
8	236.4-251.0	4.31	1.5186
9	251.0-252.7	4.41	1.5171
10	252.7-253.8	4.64	1.5170
11	253.8-253.9	4.87	1.5170
12	254.0-253.4	5.12	1.5170
13		5.45	1.5170

Refractive index at 25°C. = 1.5195
Density at 25°C. = 0.8838
Experimental molar refraction = 55.08
Calculated molar refraction = 55.31.

The higher boiling fractions, 8 through 13, Table 16, from the distillation of the olefin were believed to be unreacted alcohol.

An attempt was made to prepare the 2,4-dinitrobenzenesulfenyl chloride derivative of the lower boiling olefin. However, after recrystallizing the oil several times, the solid that was produced melted below room temperature.

DISCUSSION OF RESULTS

From the evidence already presented, it is apparent that the reaction studied gave unidentified products as well as the alcohols which were identified. Inasmuch as the impurities were also present in the derivatives of the alcohols after attempted purification of the derivatives, it would seem that the impurities are also alcohols, and are probably of approximately the same molecular weight as the alcohols identified. With this in mind the following are suggested impurities:

1. If the cumene was partially isomerized to n-propyl benzene, then reaction products of n-propyl benzene would be present.

2. If small amounts of secondary alcohols are produced by the alternate opening of the epoxide ring, then secondary alcohols should be present in the major products.

3. Ortho-substitution products should also be considered.

The identification of these impurities could assume formidable proportions. A possible attack is to prepare the products identified, as well as the materials considered as possible impurities, by methods known to yield pure compounds. A study of the infra-red spectra of these

compounds compared to the spectra of the alcohols isolated from the reaction mixtures, might serve to identify the impurities.

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